Parallel Measurements of Light Scattering and Characterization of Marine Particles in Water: An Evaluation of Methodology

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LONG-TERM GOALS

The long-term goal of our research is to develop the base of knowledge necessary to:

(i) understand the magnitudes and variability of the ocean optical properties;

(ii) predict the inherent and apparent optical properties of the ocean including remote-sensing reflectance, given the types and concentration of suspended particles;

(iii) retrieve the inherent optical properties and concentration of seawater constituents from remote sensing.

OBJECTIVES

The principal objective of this project is to evaluate various techniques for parallel (or nearly-parallel) determinations of light scattering and particle characteristics using a broad suite of experimental approaches and instruments, including both benchtop and in situ instrumentation. A second objective is to characterize variability in the volume scattering function and particle size distribution for various optical water types and samples.

Specific objectives for this reporting period include

- Complete analysis of mesocosm experiments comparing methods for measuring the volume scattering function (VSF) and the particle size distribution (PSD)

- Analysis of in situ optical measurements and particle size distributions collected from field experiments

- Perform modeling exercises to examine the influence of using simplified approximations of the PSD to predict seawater optical properties.

- Prepare a presentation for Ocean Optics Conference and a manuscript for publication.

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APPROACH

Our approach consists of experiments designed to directly compare measurements of the volume scattering function and particle size distribution on laboratory and natural particle assemblages of varying composition. For measuring the VSF, we have tested a suite of commercial instruments which measure scattering at various angles. These instruments include a Sequoia LISST-100X (32 angles, 0.08-13.5°), a Wyatt Technologies Dawn EOS (18 angles, 22.5-147°), a Wetlabs ECO-VSF (100, 125, and 150°), and a HobiLabs Hydroscat-6 (140°). All instruments utilize a light source of 532 nm, with the exception of the Hydroscat-6 which measures six spectral bands (442, 470, 550, 589, 620, and 671 nm). The combination of these instruments provides a capability for examining the VSF over a broad angular range. With regards to the particle size distribution, we have made direct comparisons of measurements using a Coulter counter, FlowCAM, LISST-100X, and a Spectrex Particle Laser Counter. Each of these instruments employs a different measurement principle of detecting and sizing particles.

A central idea underlying our approach for this project is to conduct mesocosm experiments, in which a large volume tank filled with natural water is subjected to optical and particle measurements and analyses. These experiments are designed to mimic in situ conditions, allowing "non-invasive" measurements on "unperturbed" suspended particles with a suite of instruments that are normally employed at sea. We conduct experiments with differing particle assemblages ranging from standard bead suspensions and specific types of biological particles (e.g. phytoplankton cultures) to heterogeneous assemblages of particles suspended in oceanic water samples. The sampling of natural water used in these experiments covers optically different water types within the coastal zone of San Diego, ranging from the turbid estuary of the Tijuana River to clear oligotrophic waters. To further expand the range of water types, additional field measurements are taken on cruises of opportunity.

In parallel with these tank measurements, sub-volumes of water from the tank are subjected to additional measurements with laboratory bench-top instrumentation and analytical techniques. Some of the lab methods impose no or very little alteration to particles (i.e., immediate non-invasive measurements on sub-volumes taken from the tank without any treatment of the sample) but other lab methods may alter particulate assemblages (i.e., measurements that require some kind of flow of the sample, filtration, dilution, or other treatment).

In addition to parallel mesocosm (large volume tank) and laboratory bench-top (smaller volume sub-samples from the tank) measurements, we also make in situ measurements of light scattering and particle characterization at times when samples of natural ocean water are taken for subsequent tank/lab experiments. Although only a subset of instruments can be deployed in situ, this is an important aspect of our overall approach. These in situ measurements provide a reference suite of characteristics, which allow us to examine the effects associated with water sample storage (e.g., duration, procedure/treatment during storage) between the time of sampling in the field and the time of tank and bench-top measurements in the lab.

In summary, our approach is designed to compare different types of experiments, instruments, and principles involved in the determination of light scatter and particle size distribution in order to develop an understanding of the performance of various methods that are used in oceanography for particle and light scattering characterization.

WORK COMPLETED

Our previous reports for this project describe the results of our mesocosm and in situ experiments which permit direct comparison between instruments that measure the VSF, and between instruments that measure the particle size distribution. During this reporting period, we completed overall analyses of this information and applied the findings to data collected from two field expeditions in which in situ measurements of the VSF and the PSD were measured in various coastal environments. The first expedition was conducted in Monterey Bay (MB06), and a second cruise covered coastal waters of the Baltic and North Seas (OC07). Recently (September 2008) we completed an additional series of field tests during the RaDyO field experiment in the Santa Barbara Channel; results from this cruise have not yet been analyzed. Utilizing field measurements, we conducted preliminary modeling exercises to examine how departures of the PSD from idealized approximations influence the prediction of inherent optical properties. Results from these analyses were submitted as an extended abstract for the Ocean Optics XIX conference. A manuscript that compares the various methods of PSD measurements and discusses the PSD data from the various experiments (lab, tank, and field) has been completed. We have not yet submitted this manuscript because we wish to add additional data obtained with the Coulter and LISST during a recent RaDyO cruise in the Santa Barbara Channel. These new data are highly relevant to the central theme of the manuscript.

RESULTS

The PSD exerts a strong influence on the optical properties of seawater, yet it is rarely measured in situ or in parallel with optical measurements. The LISST-100X is a commercially available instrument which estimates the PSD based upon the principle of optical diffraction [Agrawal and Pottsmith 2000], and can provide laboratory or in situ measurements at high sampling rates.

Results from our laboratory and mesocosm experiments often demonstrate a reasonably good correspondence between size distributions measured by the LISST and a Coulter counter (Fig. 1). These include suspensions of microspheres, algal cultures, and natural seawater samples taken from San Diego coastal waters. Particle concentrations, depicted here in terms of volume, are highly correlated ($R = 0.98$) between the two instruments when the PSDs are integrated over a common size range (Fig. 1A). The data suggest a systematic underestimate of particle concentration by the LISST relative to the Coulter for the microsphere suspensions, but this bias is not as evident in suspensions comprised principally of biological particles (algal cultures, field samples). For field samples, the correlation between the concentration estimated by the two instruments is extremely high ($R > 0.99$), with a median difference of 10.5%.

In addition to total concentration, we compared common descriptors of the PSD such as the median particle diameter calculated from the volume distribution (Fig. 1B). For both monodisperse and polydisperse suspensions, a reasonably good linear relationship was observed over the measured range of particle sizes. On average, the LISST underestimates the Coulter by about 12%. This bias may partially result from the coarser resolution (larger size bins) of the LISST.

Despite utilizing different principles, the LISST and the Coulter counter generally provide consistent agreement in terms of both particle size and concentration determinations. In particular, measurements on polydisperse field samples were highly correlated in terms of particle size and concentration estimates. A major exception was in the smallest size ranges ($D < 3.5$ μm), which approach the lower limit of the LISST and is an area subjected to artifacts of the inversion process [see Agrawal et al. 2008]. If the LISST data are restricted to sizes larger than this limit, it appears that reasonable estimates of the in situ PSD can be obtained with this instrument in natural waters where narrowly-sized or overlapping populations of particles have minimal contribution to the overall PSD, that is where PSD curve is relatively featureless. However, in the near future we will make further comparative analysis of the LISST and Coulter-derived PSDs based on recent measurements during the RaDyO cruise, where surface waters were characterized by the presence of several distinct populations of biological particles.

Predictive models for seawater optical properties frequently use simplified approximations of the PSD, such as the power law (Junge) model in which the number distribution $N(D) = k\,D^{-m}$. In situ measurements of the PSD obtained from the MB06 and OC07 cruises were examined within the context of this model. A power-law fit to the particle number concentration, $N(D)$, as a function of diameter D was calculated for each spectra using model I linear regression on the log-transformed data. The coefficient of determination for the fitted regressions using the log-transformed data was always high, generally ≥ 0.95. The left panel of Fig. 2 illustrates the frequency distribution of the power law exponent m obtained for each cruise. The average values of this exponent are remarkably consistent for both cruises (3.46 for MB06, 3.47 for OC07).

Previous studies in oceanic waters have reported a similar range in m, with a central value of 4 typically used for modeling the PSD in oligotrophic waters. Such values were observed in only a small subset of our data, and were primarily associated with stations located the furthest offshore and thus most oceanic in nature. The majority of our data lies in a smaller range of m, suggesting that inshore coastal waters on average have a shallower slope than offshore oligotrophic waters. This is consistent with the observation that larger particles are generally more prevalent in coastal particle assemblages, owing to an increased presence of larger planktonic species and particle aggregates.

Despite generally high values of the determination coefficients obtained when fitting the log-transformed data to the linearized power law model, examination of the residuals indicates that for any given PSD, significant deviations can occur between the observed and fitted data. In particular, certain regions of the size distribution are systematically under- or overestimated by the power law fit; for example, in the Monterey Bay dataset the power law frequently underestimates the concentration of particles in the 4 and 30 μm size range, while overestimating concentrations in the 10 μm size range. It should also be noted that any given PSD can have much higher biases, in some cases concentrations within a given size class were observed to be understimated by nearly 3 orders of magnitude. These situations were almost always associated with distinctive peaks in the PSD, resulting from local blooms of a given plankton population, which are not captured by a monotonic approximation to the PSD. The residuals of the observed PSD from the fitted PSD can be used to identify distinctive particle populations and to examine their distributions in the water column (Fig. 2, right panel).

Inherent optical properties such as the spectral absorption and scattering coefficients of seawater strongly depend upon both the size distribution of suspended particles and their refractive index. Forward models of seawater optical properties attempt to predict radiative transfer within the ocean from detailed knowledge of the particle assemblage concentration and composition [e.g. Stramski et al. 2001]. Inversions of such models can also be used to derive information on the particle assemblage from measured optical properties [Twardowski et al. 2001]. Because the PSD is rarely measured in field studies, it is generally modeled using empirical formulations with varying degrees of complexity.

Our measurements in coastal waters suggest that departures from these idealized models occur frequently, and can have a large influence on the accuracy of predicted optical properties.

To examine the potential influence of the PSD on such calculations, we have coupled our PSD measurements with Mie computations of light scattering and absorption by particles. Inputs to the model include the particle size distribution and the complex refractive index. We assume that particles are spherical and homogenous, and a constant refractive index for all size classes. As our intent is to simply examine potential effects of the PSD on light attenuation, these assumptions can be reasonably adopted for the purpose of identifying general trends.

Several particle size distributions of surface waters were chosen from the LISST database of measurements collected at different locations. Representative stations were selected to cover different scenarios, for example stations in which the PSD was relatively featureless and well-approximated by a power law function, as well as locations which exhibited significant departures from this behavior owing to the presence of one or more peaks in the distribution. Measured PSDs were fit to a power-law model as described previously, and the derived coefficients were used to generate a modeled PSD. The total concentration of particles within the measured size range, $\Sigma N(D)$, and the mean cell projected area, G, were computed for each measured and modeled size distribution.

Both measured and modeled PSDs were used as input for the computation of absorption and scattering functions utilizing the code of Bohren and Huffman [1983] modified to include the effects of polydispersion. A light wavelength of 550 nm was used in these calculations, and a particle refractive index of 1.05+0i was assumed for all particles. Outputs of these computations yielded the mean efficiency factor for attenuation, $Q_c(550)$. The predicted beam attenuation coefficient of particles was then calculated for both observed and modeled size distributions as

$$c_p(550) = \Sigma N(D)\ G\ Q_c(550) = \Sigma N(D)\ \sigma_c(550)$$

where σ_c represents the mean particle attenuation cross-section.

Table 1 illustrates example results of such computations for the two PSDs depicted in Fig. 3. A relatively good agreement between measured and modeled c_p was observed at some stations, represented here by the sample I2002. The PSDs at such locations are reasonably well-described by a power law model, and correspond to the most offshore extent of our stations and are thus most representative of oceanic conditions. In these cases predicted total particle concentrations are similar to the observed values. Both the mean projected area and the modeled efficiency factor are slightly underestimated by the modeled PSD, such that the computed attenuation cross-sections compensate for the slight overestimation of particle concentration.

The sample IBP22 is an example in which the modeled c_p is significantly lower than the observed value. This location was sampled during the presence of a “red tide”, in which a dinoflagellate species was abundant in high concentrations. The observed size distribution is characterized by a broad prominent peak in the size range of 35 μm. The power law model obviously does not reproduce this peak, but its presence influences the fit so that particle concentrations are overestimated in both smaller and larger size classes and results in an overestimate of $\Sigma N(D)$. The absence of the peak in the modeled distribution leads to significant underestimation of the calculated mean projected area of the population, overestimation of Q_c to a lesser extent, and thus the cross-section as a whole is underestimated. The combined errors of overestimating particle number and underestimating the mean cross-section compensate each other to some degree, but the calculated c_p is still underestimated by a significant amount.

The results of this simple exercise indicate that the use of simplified models for the particle size distribution can result in significant errors in the estimation of bulk optical properties. The magnitude of the prediction error is often reduced to some extent through opposite trends in the prediction of particle number and the optical cross-section. These errors are most pronounced when the PSD deviates from a power-law because of significant curvature, or the presence of significant peaks resulting from increases in an individual size range. Both of these features are not uncommon features in coastal waters.

IMPACT/APPLICATIONS

The major impact of this project will be to provide an evaluation of the performance of various methods for estimating the volume scattering function and the particle size distribution, characterization of their advantages and disadvantages, and quantification of errors and limitations of individual methods. Based on results of our experiments, we are developing a set of recommendations and improved protocols for the use of various techniques to estimate light scatter and particle characterization. In addition, data generated during this project will contribute to the science of the quantification and understanding of marine particle properties.

RELATED PROJECTS

The coastal zone of San Diego offers an opportunity to examine diverse water types with varying particle assemblages, from the turbid estuary of the Tijuana River to clear oligotrophic ocean water. As part of a NASA funded project, we sampled coastal waters on a regular basis to examine temporal trends in seawater particles and optical properties. The availability of these samples for instrument comparisons, and the extra biological and chemical information they provide about particle assemblages, increases our ability to build a database for comparisons of direct interest to this project.

Other projects and cruises of opportunity in which we have collected additional field data relevant to this project include a north-south transect in the eastern Atlantic (ANT-XXIII/1, NASA), Monterey Bay (COAST experiment, NOAA), an expedition in the Baltic and North Sea, and the recent ONR RaDyO field experiment in the Santa Barbara Channel.

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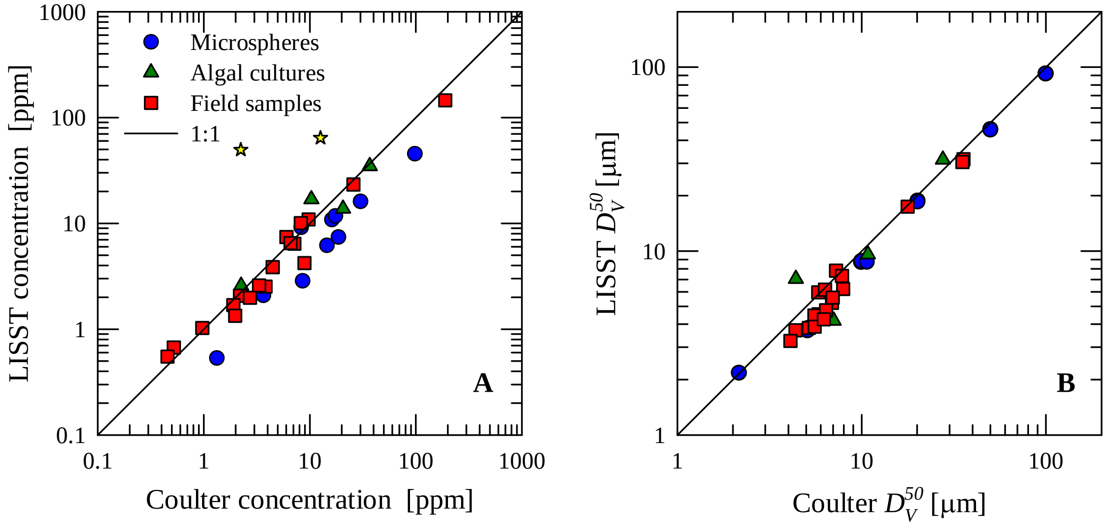

Figure 1. Scatter plots comparing particle concentration (A) and median diameter (B) derived from size distributions measured with both a Coulter counter and a LISST-100X. Three types of particle suspensions are depicted; polystyrene microspheres, monospecific cultures of marine phytoplankton, and natural seawater samples collected at different times of the year from Imperial Beach and Scripps Pier. The two starred samples in panel A represent experiments with 100 µm microspheres, from which reliable concentration estimates could be obtained owing to difficulty in maintaining the particles in suspension.

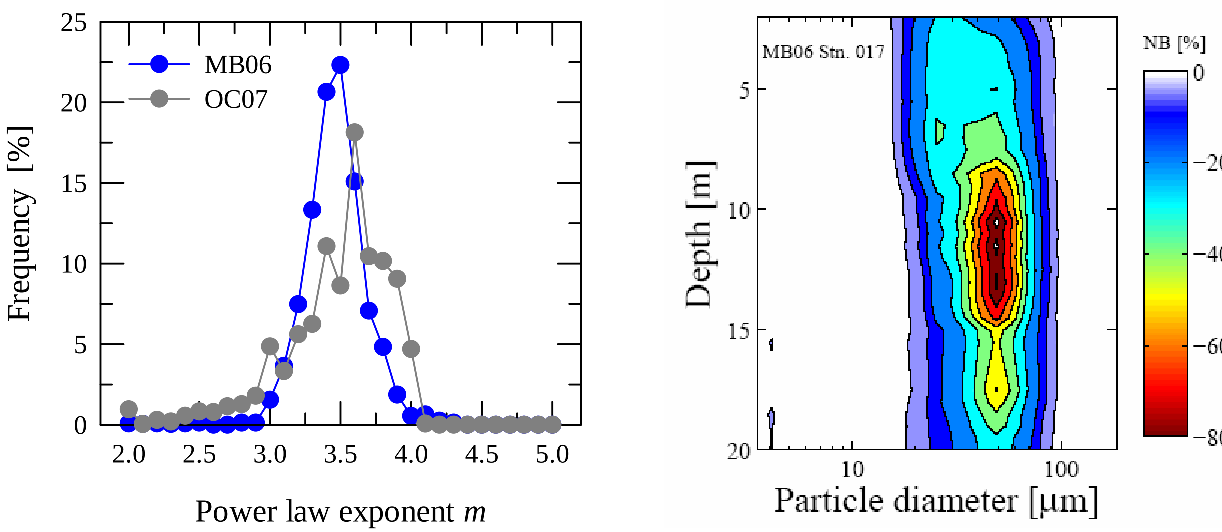

Figure 2. (Left panel) Frequency distribution of the power law exponent m for particle size distributions measured on MB06 (N=2408) and OC07 (N=3074) cruises. The data include all sampling depths. (Right panel) Residuals in each size class between the measured PSD and the overall power law fit to the data as a function of depth for a station in Monterey Bay. The residuals are depicted as normalized bias between fitted and observed particle concentration ((Fit – Obs.)/Obs.) in percent.

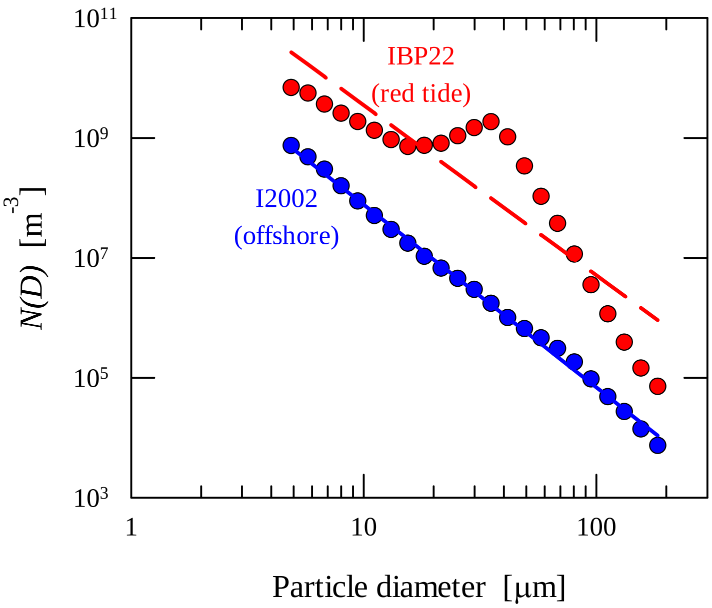

Figure 3. Two PSDs used as examples for the Mie modeling exercise (see Table 1). Size distributions measured in situ are shown for each station (circles), as well as power law fits to the observed data (lines).

Table 1. Example results of calculations to estimate the potential impact of using modeled particle size distributions in calculations of suspension optical properties. For each station, two PSDs were used as input to Mie scattering calculations; the observed PSD and a modeled PSD derived from fitting the observed data to a power-law function (see Fig. 3 above). The table lists values of the integrated particle concentration $\Sigma N(D)$, the mean projected area G, the mean efficiency factor for beam attenuation Q_c, and the predicted particle beam attenuation coefficient c_p calculated for both PSDs. The Mie calculations assume a light wavelength of 550 nm, and a complex index of refraction for particles of 1.05 + 0i. The percent difference between the observed and modeled PSD is given for each parameter.

	$N(D)$ x 10^{-9}, [m^{-3}]			G, [μm^2]			Q_c(550), [dim]			c_p(550), [m^{-1}]		
Stn.	Obs.	Mod.	%	Obs.	Mod.	%	Obs.	Mod.	%	Obs.	Mod.	%
I2002	4.516	4.748	5.1	31.7	30.3	-4.5	2.60	2.56	-1.3	0.37	0.37	-0.9
IBP22	30.955	71.419	130.7	307.3	66.1	-78.5	2.08	2.43	17.1	19.74	11.47	-41.9